4 31-L-12 EPA 89/2:600/54-85/082

United States
Environmental Protection
Agency

Environmental Monitoring Systems
Laboratory
Las Vegas NV 89114

Research and Development

EPA/600/S4-85/082 Jan. 1986

EPA

Project Summary

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Single-Laboratory Evaluation of the RCRA Method for Analysis of Dioxin in Hazardous Waste

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ORIGINAL

Single laboratory testing of RCRA Method 8280 for the determination of chlorinated dibenzo-p-dioxins and -furans has been initiated on sample matrices including pottery clay, Missouri soil, fly ash, a still bottom from a chlorophenol-based herbicide production process, and an industrial process sludge. This method was intended for the analysis of chlorinated dioxin and dibenzofuran homologs with four, five, or six chlorine atoms per molecule. Revisions to the method, which were found necessary for satisfactory performance, have been tested and incorporated into a revised version of the method.

Single laboratory testing of Method 8280 incorporating minor revisions provided satisfactory performance for the target analytes in soil and fly ash samples. Further modification and elaboration of sample cleanup procedures were necessary for the analysis of the still bottom and industrial sludge samples.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In part, as a result of finding trace levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) as a contaminant in commercial preparations of chlorophenol-based herbicides, the U.S. EPA initiated (in 1973) monitoring efforts for 2,3,7,8-TCDD in environmental samples. Later findings of contamination by 2,3,7,8-TCDD in soil samples from Niagara Falls, New York, and various sites in Missouri led to extensive sampling and analysis efforts. It is now known that many, if not all, of the 75 possible chlorinated dioxins and 135 structurally related chlorinated dibenzofurans possess relatively high toxicities to man and certain animal species. Most available acute and chronic toxicological data for chlorinated dioxins and dibenzofurans are based upon the 2,3,7,8-TCDD isomer. In certain animal species (notably, the guinea pig), extraordinarily low doses may be lethal. As such, these compounds are considered to be among the most potent man-made toxicants. Exposure to these compounds has been observed to produce a wide range of systemic effects including hepatic disorders, carcinoma, and teratogenicity in certain animal species, although the major documented effect upon humans has been chloracne.

The EPA has determined that enhanced toxicities are likely to be observed with samples containing tetra-, penta-, and hexa-chlorinated dioxins and dibenzofurans (40 CFR 261, 1978, January 14, 1985). In 1983 (40 CFR 65, 14514, April 4, 1983), the EPA proposed a ruling affecting disposal of hazardous wastes containing tetra-, penta-, and hexa-chlorinated dioxins and dibenzofurans. These

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wastes would be managed under the Resource Conservation and Recovery Act (RCRA) and would be analyzed for the target chlorinated dioxins and dibenzofurans using an analytical method which was included as an Appendix to the proposed rule.

In order to manage these wastes effectively, it is necessary to obtain data regarding the performance of the method included in the Federal Register on relevant waste samples. This study was intended to determine and elaborate any changes needed for satisfactory method performance and to provide method performance data after any revisions had been made. Hazardous waste sample matrices which have been subjected to analysis under this method include soils, a carbonaceous material (fly ash), a chlorophenol production still bottom, and an industrial sludge.

This report summarizes results obtained under a single-laboratory evaluation. The final revised method has been shown to perform well on a number of sample types.

Study Design

RCRA Method 8280 for the analysis of chlorinated dibenzo-p-dioxins and dibenzofurans consists of 4 major sections: (1) extraction of the analytes from the sample; (2) "open" column chromatographic cleanup with alumina using a methylene chloride/hexane eluent; (3) HPLC cleanup; and (4) analysis by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS). In order to test the method and to develop appropriate modifications with minimal redundancy, each section of the procedure was tested separately. Initial tests were performed on a simple (pottery clay soil) sample matrix and upon standard solutions. Only after adequate method performance data was achieved on such materials, was the analysis of more complex samples investigated. The first step to be elaborated was the measurement technique. Both HRGC/LRMS and HRGC/ECD (electron capture detection) were tested, using guidelines from the published RCRA method. Given the requirements of the detector, the cleanup steps were then studied in detail and appropriate modifications were investigated and documented. Additional evaluation of this method involved a systematic investigation of each critical phase. This procedure allowed for a separate description of each section of the method to document any recommended modification.

Results

The principal types of revisions which were made to the original method include: (1) the addition of a carbon column cleanup procedure to eliminate closely related chemical species; (2) revision of the alumina column elution pattern so that all desired analytes eluted in a single fraction, with the bulk of the analytical interferences removed; (3) changes in the sample preparation procedures so that wet samples could be accommodated; and (4) addition of HPLC procedures that could be reproducibly and effectively performed.

The RCRA method with revisions discussed above, was subjected to performance tests which included (1) analysis of reference materials containing 2,3,7,8-TCDD and interferences; (2) precision and accuracy determinations on samples having known composition obtained by spiking the sample matrix.

Performance of the revised method was documented through precision and accuracy determinations (standard deviation of results), by recovery of spiked analytes and isotopically-labeled standards, and by using two independent teams of analysts.

After incorporating necessary revisions, satisfactory method performance has been demonstrated on RCRA type samples. Performance of the method on relativley complex matrices, such as sludges, still bottoms, and fly ash, has been determined and precision and accuracy data are summarized in Tables 1 and 2.

Table 1. Precision Data for Revised Method 8280

Compound	Matrix[1]	Analyte Level (ng/g) Native	Native + Spike	N	Percent RSD
2,3,7,8-TCDD	clay	ND[2]	5.0	4	4.4
	soil	378	378	4	2.8
	sludge	ND	125	4	4.8
	fly ash	ND	46	2	--
	still bottom	487	487	4	24
1,2,3,4-TCDD	clay	ND	5.0	3	1.7
	soil	ND	25.0	4	1.1
	sludge	ND	125	4	9.0
	flyash	38.5	38.5	4	7.9
	still bottom	ND	2500	4	--
1,3,6,8-TCDD	clay	ND	2.5	4	7.0
	soil	ND	25.0	4	5.1
	sludge	ND	125	4	3.1
	fly ash	19.1	19.1	2	--
	still bottom	227	2727	2	--
1,3,7,9-TCDD	clay	ND	2.5	4	19
	soil	ND	25.0	4	2.3
	sludge	ND	125.0	4	6.5
	fly ash	58.4	58.4	2	--
	still bottom	ND	2500	2	--
1,3,7,8-TCDD	clay	ND	5.0	4	7.3
	soil	ND	25.0	4	1.3
	sludge	ND	125	4	5.8
	fly ash	16.0	16.0	4	3.5
	still bottom	422	2920	2	--
1,3,7,8-TCDD	clay	ND	5.0	4	7.7
	soil	ND	25.0	4	9.0
	sludge	ND	125	4	7.7
	fly ash	2.6	2.6	3	23
	still bottom	ND	2500	2	--
1,2,8,9-TCDD	clay	ND	5.0	4	10
	soil	ND	25.0	4	0.6
	sludge	ND	125	4	1.9
	fly ash	ND	46	2	--
	still bottom	ND	2500	2	--
1,2,3,4,7-PeCDD	clay	ND	5.0	4	10
	soil	ND	25.0	4	2.8
	sludge	ND	125	4	4.6
	fly ash	25.8	25.8	2	6.9
	still bottom	ND	2500	2	--

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Table 1. *(Continued)*

Compound	Matrix[1]	Analyte Level (ng/g) Native	Native + Spike	N	Percent RSD
1,2,3,7,8-PeCDD	clay	ND	5.0	4	25
	soil	ND	25.0	4	20
	sludge	ND	125	4	4.7
	fly ash	ND	46	2	--
	still bottom	ND	2500	2	--
1,2,3,4,7,8-HxCDD	clay	ND	5.0	4	38
	soil	ND	25.0	4	8.8
	sludge	ND	125	4	3.4
	fly ash	ND	46	2	--
	still bottom	ND	2500	2	--
1,2,3,4,6,7,8-HpCDD	clay	ND	5.0	4	--
	soil	ND	25.0	4	--
	sludge[3]	8760	8780	4	--
	fly ash	ND	--	--	--
	still bottom	ND	--	--	--
1,2,7,8-TCDF	clay	ND	5.0	4	3.9
	soil	ND	25.0	4	1.0
	sludge	ND	125	4	7.2
	fly ash	7.4	7.4	3	7.6
	still bottom	ND	2500	2	--
1,2,3,7,8-PeCDF	clay	ND	5.0	4	6.1
	soil	ND	25.0	4	5.0
	sludge	ND	125	4	4.8
	fly ash	ND	46	2	--
	still bottom[3]	25600	28100	2	--
1,2,3,4,7,8-HxCDF	clay	ND	5.0	4	26
	soil	ND	25.0	4	6.8
	sludge	13.6	139	4	5.6
	fly ash	24.2	24.2	4	13.5
	still bottom	ND	2500	2	--
OCDF	clay	ND	--	--	--
	soil	ND	--	--	--
	sludge	192	317	4	3.3
	fly ash	ND	--	--	--
	still bottom	ND	--	--	--

[1]*matrix types:*

clay: pottery clay, Westwood Ceramic Supply Co., City of Industry, California.

soil: Times Beach, Missouri. Soil was blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator designated as resource recovery ash No. 1.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production obtained from Arthur D. Little, Inc., 1983.

sludge: sludge from cooling tower which received both creosote and pentachlorophenolic wastewaters.

Cleanup of clay, soil and fly ash samples was through the alumina column only. (Carbon column not used.)

[2]*ND—not detected at concentration injected (final volume 0.1 ml or greater).*

[3]*Estimated concentration out of calibration range of standards.*

Matrix Analysis

A pottery clay sample was selected as a model matrix for determining extraction efficiency obtained following the recommended method. A 50 ng spike of 2,3,7,8-TCDD was added, and extraction was performed as specified in the unrevised method. This experiment was performed in triplicate, and a similar experiment was performed in triplicate on wet pottery clay (i.e., 5.0 g clay, and 5.0 g water). Performance of the extraction procedure was poor, therefore, a modified extraction solvent system was developed. This modified procedure adds methanol and sodium sulfate to the petroleum ether solvent specified in the method and uses a Kuderna-Danish concentration technique. Performance was improved on both dry and wet samples and the revised extraction procedure resulted in satisfactory overall method performance (e.g., dioxin surrogate spike recovery values).

A representative sample of pottery clay was spiked with suitable interferences and with analytes of interest (PCDD's and TCDF) to determine method performance on a clean soil matrix. Interferences such as Silvex, DDE, and Aroclor 1260 were used at concentrations from 10 to 200 times that of each target analyte. Separation of interferences in clay samples was achieved.

A portion of a municipal incinerator fly ash material was obtained in order to provide an environmental carbonaceous type matrix for testing. This type of sample historically has required toluene or benzene extraction with a Soxhlet apparatus to remove absorbed dioxins nd dibenzofurans. These analytes are often found in such samples at high ppt to low ppb levels. Therefore, it was decided to spike such a sample with $^{13}C_{12}$-2,3,7,8-TCDD and analyze by revised Method 8280. At the worst, a synthetic dioxin sample would be characterized, and at the best, a quantitative analysis would be performed to determine the levels of environmentally-incorporated dioxins and furans, using an isotopically-labeled TCDD internal standard. Results of the HRGC/LRMS analysis indicated the presence of numerous "native" PCDD's and PCDF's, in addition to a variety of other compounds at higher levels. Recovery of the isotopically labeled TCDD (spiked into the sample at a concentration to 500 pg/g) was 90 percent, using toluene/Soxhlet/revised Method 8280.

A still bottom sample from a chlorophenol production process was obtained for use as a complex waste sample. The sample had been characterized by an independent laboratory, which reported detectable concentrations of some PCDD's and PDCF's. Historically, these samples have been most difficult to analyze for dioxins and dibenzofurans. Due to presence of massive amounts of analytical interferences, poor reproducibility, low recovery of spiked PCDD's and PCDF's,

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Table 2. *Recovery Data for Revised Method 8280*

Compound	Matrix[1]	Native[2] (ng/g)	Spiked[3] Level (ng/g)	Mean Percent Recovery
2,3,7,8-TCDD	clay	ND	5.0	61.7
	soil	378	--	--
	sludge	ND	125	90.0
	fly ash	ND	46	90.0
	still bottom	487	--	--
1,2,3,4-TCDD	clay	ND	5.0	67.0
	soil	ND	25.0	60.3
	sludge	ND	125	73.1
	fly ash	38.5	46	105.6
	still bottom	ND	2500	93.8
1,3,6,8-TCDD	clay	ND	2.5	39.4
	soil	ND	25.0	64.0
	sludge	ND	125	64.5
	fly ash	19.1	46	127.5
	still bottom	227	2500	80.2
1,3,7,9-TCDD	clay	ND	2.5	68.5
	soil	ND	25.0	61.3
	sludge	ND	125	78.4
	fly ash	58.4	46	85.0
	still bottom	ND	2500	91.7
1,3,7,8-TCDD	clay	ND	5.0	68.0
	soil	ND	25.0	79.3
	sludge	ND	125	78.9
	fly ash	16.0	46	80.2
	still bottom	615	2500	90.5
1,2,7,8-TCDD	clay	ND	5.0	68.0
	soil	ND	25.0	75.3
	sludge	ND	125	80.4
	fly ash	2.6	46	90.4
	still bottom	ND	2500	88.4
1,2,8,9-TCDD	clay	ND	5.0	59.7
	soil	ND	25.0	60.3
	sludge	ND	125	72.8
	fly ash	ND	46	114.3
	still bottom	ND	2500	81.2
1,2,3,4,7-PeCDD	clay	ND	5.0	58.4
	soil	ND	25.0	62.2
	sludge	ND	125	79.2
	fly ash	25.8	46	102.4
	still bottom	ND	2500	81.8
1,2,3,7,8-PeCDD	clay	ND	5.0	61.7
	soil	ND	25.0	68.4
	sludge	ND	125	81.5
	fly ash	ND	46	104.9
	still bottom	ND	2500	84.0
1,2,3,4,7,8-HxCDD	clay	ND	5.0	46.8
	soil	ND	25.0	65.0
	sludge	ND	125	81.9
	fly ash	ND	46	125.4
	still bottom	ND	2500	89.1
1,2,3,4,6,7,8-HpCDD	clay	ND	5.0	ND
	soil	ND	25.0	ND
	sludge[4]	8780	125	--
	fly ash	ND	--	--
	still bottom	ND	--	--
2,3,7,8-TCDD (C-13)	clay	ND	5.0	64.9
	soil	ND	25.0	78.8
	sludge	ND	125	78.6
	fly ash	ND	46	88.6
	still bottom	ND	2500	69.7

and relatively poor detection limits are common. Nonetheless, this challenging sample represents a sample type likely to be encountered as a RCRA waste. This sample may be described as having effectively *totally* potential interferences, since it dissolved in toluene readily, and at least partially in hexane. Full-scan HRGC/LRMS using a 30 m DB-5 nonpolar column was performed in order to obtain partial sample characterization. Through this work and later multiple ion detection (MID) HRGC/LRMS studies using CP-Sil-88 and SP-2250 columns, chlorinated phenols, diphenyl ethers, and hydroxydiphenylethers ("pre-dioxins") were found, along with the target analytes. Apparently it is common on all GC columns tested for dioxins, dibenzofurans, and diphenyl ethers to co-elute, complicating the mass spectral analysis. Careful interpretation of spectra and retention times of standards is necessary to avoid misidentifying diphenyl ethers, benzylphenyl ethers, or hydroxydiphenylethers having similar m/z ion clusters as target PCDD's or PCDF's.

Because of the limited success of the revised RCRA Method 8280 towards analysis of this sample, an additional cleanup step, using a silica Spherisorb/PX-21 charcoal column was incorporated into the procedure. With this modification acceptable recoveries and precision were obtained for even the most complex samples.

A sludge sample was obtained by the EPA from a cooling tower which receives both creosote and pentachlorophenolic wastewaters. This sample contained a high percentage of water (76 percent) and rivaled the chlorophenol still bottom sample in complexity of the solvent extractable organic fraction. The water was removed by azeotropic distillation with toluene and the toluene extract was then used for analysis of the PCDD's and PCDF's. This extract was cleaned up using the modified RCRA Method 8280 procedure, which included the use of the silica Spherisorb/PX-21 charcoal column.

This study has been completed on a limited number of matrix and sample types; the results show that the revised Method 8280 provides good recovery of the internal standard, $^{13}C_{12}$ - 2,3,7,8 - TCDD and the target PCDD and PCDF analytes. The proposed cleanup procedures were shown to be effective in dealing with complex matrix problems. An interlaboratory comparison study of the revised method is expected to provide additional method performance information.

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Table 2. *(Continued)*

Compound	Matrix[1]	Native[2] (ng/g)	Spiked[3] Level (ng/g)	Mean Percent Recovery
1,2,7,8-TCDF	clay	ND	5.0	65.4
	soil	ND	25.0	71.1
	sludge	ND	125	80.4
	fly ash	7.4	46	90.4
	still bottom	ND	2500	104.5
1,2,3,7,8-PeCDF	clay	ND	5.0	57.4
	soil	ND	25.0	64.4
	sludge	ND	125	84.8
	fly ash	ND	46	105.8
	still bottom	25,600	2500	--
1,2,3,4,7,8-HxCDF	clay	ND	5.0	54.2
	soil	ND	25.0	68.5
	sludge	13.6	125	82.2
	fly ash	24.2	46	91.0
	still bottom	ND	2500	92.9
OCDF	clay	ND	--	--
	soil	ND	--	--
	sludge	192	125	86.8
	fly ash	ND	--	--
	still bottom	ND	--	--

[1]*matrix types:*

clay: pottery clay, Westwood Ceramic Supply Co., City of Industry, California.

soil: Times Beach, Missouri. Soil was blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator designated as resource recovery ash No. 1.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production obtained from Arthur D. Little, Inc., 1983.

sludge: sludge from cooling tower which received both creosote and pentachlorophenolic wastewaters.

The clay, soil and fly ash samples were subjected to alumina column cleanup, no carbon column was used.

[2]*Final volume of concentrate 0.1 ml or greater, ND means below quantification limit, 2 or more samples analyzed.*

[3]*Amount of analyte added to sample, 2 or more samples analyzed.*

[4]*Estimated concentration out of calibration range of standards.*

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The complete report, entitled "Single-Laboratory Evaluation of the RCRA Method for Analysis of Dioxin in Hazardous Waste," (Order No. PB 86-135 175/AS; Cost: $16.95, subject to change) will be available only from:

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